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Polymerization, shock cooling and ionization of liquid nitrogen

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Abstract

The trajectory of thermodynamic states passed through by the nitrogen Hugoniot starting from the liquid and up to 10^6 GPa has been studied. An earlier report of cooling in the doubly shocked liquid, near 50 to 100 GPa and 7500 K, is revisited in light of the recent discovery of solid polymeric nitrogen. It is found that cooling occurs when the doubly shocked liquid is driven into a volume near the molecular to polymer transition and raising the possibility of a liquid-liquid phase transition (LLPT). By increasing the shock pressure and temperature by an order of magnitude, theoretical calculations predict thermal ionization of the L shell drives the compression maxima to 5-6 fold compression at 10 Mbar (T~3.5 10^5 K) and at 400 Mbar (T~ 2.3 10^6 K) from K shell ionization. Near a pressure of 10^6 GPa the K shell ionizes completely and the Hugoniot approaches the classical ideal gas compression fourfold limit.

I. Introduction

A fundamental principle of chemical physics is that pressure-induces electron delocalization leading to new structures with very different thermal and mechanical properties. Very high temperatures and pressures produce dense plasmas and fully delocalized electrons. In the case of nitrogen the large binding energy of the N_2 triple bond makes it one of the most stable and difficult to modify, and a particularly strong challenge to theorists and experimentalists. Theoretical calculations based on local-density-functional theory (LDT) total energy methods predict that increasing the pressure destabilizes the triple bond leading to the formation of a polymeric cubic-gauche (c-g) structure in which each atom is connected to by single *sp* bond to three neighbors [1-4]. Predicted transition pressures were in the range near 50-75 GPa, lower than recently determined experimentally [5-8] due to a large energy barrier.

Optical evidence for a non-molecular semi-conducting (possibly amorphous) phase of nitrogen was obtained by Goncharov et al.[5] and Eremets et al.[6], at a pressure above 150 GPa, using the diamond-anvil-cell (DAC) technique. Subsequently, the transformation of molecular nitrogen to the single-bonded cubic-gauche form was achieved by Eremets et al.[7,8] near 110 GPa. In order to synthesize this phase, the hysteresis barrier effects were overcome by heating in a DAC to a temperature of 2000 K.

In comparison with diamond-cell experiments, shock experiments have the capability for achieving simultaneously very high pressures and temperatures, are therefore well suited to examine the higher energy states of condensed nitrogen. Shockwave measurements made for the liquid nitrogen Hugoniot using a two-stage light-gas gun have been reported by Radousky et al.[9] and Nellis et al.[10]. In addition to the single shock states they reported reflected, or second shock, measurements in which they observed the unusual feature of shock cooling. Using the light-gas gun to achieve quasi-isentropic compression, Chau et al.[11] measured electrical conductivities for fluid nitrogen which showed evidence for a nonmetal-metal transition near 120 GPa, at a temperature estimated at 7000 K.

Mattson et al[4] have reported results of calculations for the cubic-gauche, and for additional phases competitive with the crystalline diatomic structure. However, Mattson went further and searched for possible structures in the dense liquid by carrying out LDT-molecular dynamic simulations for cells of 64 atoms at temperatures up to 10,000 K, and identified characteristic structures by quenching. This led to their finding mixtures in the liquid of three-fold coordinated atoms (cubic-gauche-like) and two-fold coordinated chain-like structures. These calculations were made at temperatures and densities near where shock cooling had been reported by Nellis et al. [10].

The work presented in this paper was motivated largely by the possibility that shock cooling in liquid nitrogen, and polymer formation in the solid are tied closely by key elements in the electronic structure, particularly *sp* covalent bonding. In earlier publications [12,13] it was proposed that shock cooling in liquid nitrogen was a consequence of polymer formation. Although the term polymer was not employed specifically at that time, the conclusion drawn was

that the cause of cooling was that N_2 dissociated into a more highly coordinated covalently bonded state in common with the higher Z elements in Group V. In Section II, our earlier study on shock compressed liquid nitrogen l12,13] is reexamined with respect to the new experimental and theoretical work cited above. In Section III we extend our study to the nitrogen Hugoniot to much higher temperatures and pressures, into the dense plasma regime, where the covalently bonded molecular systems are fully dissociated into atoms and ionized to form dense plasmas. Section IV is the Discussion.

II. Nitrogen polymers and reflected shock cooling.

The principal Hugoniot and shock temperatures, for liquid nitrogen have been measured to nearly 100 GPa using the LLNL two-stage light gas gun[9,10]. This data is shown in figure 1. The studies included five doubly or second shocked points starting from different initial pressures along the principal single shock Hugoniot. In a double shock experiment the first shock is reflected back off of a stiff end plate material such as copper. By measuring the shock velocity in the end plate and impedance matching with the equation of state of the liquid nitrogen the pressure and density of the doubly shocked liquid can be determined. Hence a doubly shocked point is often referred to as a reflected shock point or a second shock. The numerals in figure 1 indicate double shocking from first to second shocks points (i.e., 1 to 1. etc.). The dashed lines show three of the calculated reflected shock trajectories made using the theoretical model described below. In the lower right hand corner of the figure we have denoted the region in the phase diagram where Erements [3] synthesized c-g polymeric nitrogen.

A. Free energy model of compressed liquid nitrogen

In order to examine and explain the physics of reflected shock cooling, a semi-empirical two-state fluid mixture model was developed [12,13]. The pure N_2 liquid ground state is modeled with soft-sphere liquid theory using an exponential-six intermolecular potential that was fitted to the solid isotherm. In modeling the higher energy state, logic argues that since dissociation to atoms by breaking three bonds required about 9.9 eV, this was highly unlikely at the

ambient shock temperatures (Fig.1). In analogy with the other group V elements, phosphorous and arsenic, it was assumed that N_2 should dissociate into a more highly coordinated covalently bonded state, or in the current parlance -- a polymer.

Lacking the theoretical insight, which was later provided by the future electron band theory results of Mailhiot[2], the nitrogen polymer used in the model was defined only in terms of an empirical expression employed to back out insight from the experimental shock data, a form of reverse theory. The free energy of the model is written in terms of a linear mixture of N_2 molecules and of N atoms bonded in some undefined form. We write the free energy, per two atoms, as;

$$F = (1 - x)F^o_{N_2} + A_{\text{int}} + F_{mix} + x(F^o_{2N} + D_e + E_b). \qquad (1)$$

The first term is the free energy of an isolated molecule, including internal degrees of freedom, but not including the dimer bond energy. x is the fraction of the dissociated dimers calculated by minimizing the free energy. A_{int} is the thermal free energy of the total mixture. Since a knowledge of the inter N-polymer force law was, and is still lacking it was assumed that the atom-atom repulsive forces of non-bonded atoms in molecular N_2 and in N-polymer systems remained unchanged. Therefore the thermal free energy of the dense fluid mixture, A_{int}, determined by intermolecular forces remains unchanged upon dissociating from N_2 to an N-liquid. F_{mix} is the free energy of mixing.

The last term on the RHS of eq.1 as written describes the free energy needed to create the polymer state as a sequential process. First to free atoms at an energy cost of D_e =9.91 eV, but with a return of E_b in bonding energy to form a covalently bonded "N-polymer". We chose E_b as

$$\begin{aligned} E_b &= -A(V_0 - V)^2, \qquad V < V_0, \\ E_b &= 0, \qquad V > V_0. \end{aligned} \qquad (2)$$

Model parameters A and V_o were adjusted to best fit all the shock data [12]. An effective dissociation energy may be defined as,

$$D = D_e + E_b\ , \qquad (3)$$

the energy needed to break the dimer bond and form a polymer molecule. Unlike the dissociation energy of the gas, D is volume dependent. The form of the

binding energy E_b , in eq. 2, was determined empirically by finding that shock cooling would occur only if D were forced to decrease quadratically to a closure value (D=0) at high density. This feature is consistent with the subsequent *ab-initio* LDA calculations of Mailhiot et al.[2] shown in figure 2.

Plotted in figure 2 are the energy-volume curves, of the linear chain, *c-g* and *A7*, and that of the N-polymer model phase described by eqs. 2 and 3. The N-polymer phase lies the higher in energy, having been determined from a fit to the high temperature liquid shock data. The LDT calculations were made for solids in a periodic lattice, while the shocked liquid likely consists of a mixture of polymer fragments or polymorphs so that eq. 2 represents the energy of an "average" polymer fragment. As for example, the finding by Mattson of mixtures in the liquid of three-fold and two-fold coordinated atom structures[4]. However, the most significant feature here is that with decreasing volume the energy of all the polymers decrease relative to the N_2 solid. This is consistent with a continuous evolution from a primarily *sp*-bonded structure to sp^2-like and to sp^3-like as a function of pressure. The closure volume, D=0, in the model was determined to be 5 $Å^3$/atom in reasonable agreement with the electron band theory predictions [2].

Since E_b is a temperature independent term, at T=0 K the total energy of the N-polymer solid is,

$$E_{N\text{-}solid} = E_{N_2} + D. \qquad (4)$$

E_{N_2} is the energy of N_2 solid. It follows that the pressure of N-polymer solid can be written as,

$$P_{N\text{-}sold} = P_{N_2} - \partial D/\partial V. \qquad (5)$$

Figure 3, shows the P-V isotherm of nitrogen measured by Eremets et al.[8] in which they found a close-packed N_2 to cg-N transition to occur at 110 GPa with a volume change from 6.7$Å^3$ to 5.2 $Å^3$. The solid curves were calculated using the model described above. The pressure of the *cp* solid phase, P_{N_2}, was calculated with the exponential-six potential used in the Hugoniot calculations, and the pressure of the solid polymer phase was calculated using eqs. 2-5,[12]. The calculated model isotherms are in good agreement with the experimental measurements [8].

B. Polymeric nitrogen

From a purely thermodynamic point of view, shock induced cooling may be understood by considering the Grüneisen parameter,

$$\gamma = V(\partial P/\partial E)_v = (V/C_v)(\partial P/\partial T)_v. \qquad (5)$$

For most materials, $\partial P/\partial E$, $\partial P/\partial T$, and γ have positive values. A negative $(\partial P/\partial T)_v$ implies that in the P-T plane, higher temperature isotherms will lie below those with lower temperatures. The origin of negative γ values may be understood by first examining the shapes of the energy-volume curves, plotted in figure 2. The curves in figure 2 show that with decreasing volume the energy of the polymer decreases relative to the energy of N_2 solid. In other words the energy gap decreases with decreasing volume. As a result, the creation of a polymer from the N_2 solid by the absorption of shock kinetic energy leads to a pressure lowering ($dP/dE < 0$) and a negative Grüneisen parameter for this process. With decreasing volume this process is intensified by the narrowing energy gap that increases the amount of N_2 dissociation accompanied by polymer formation, making an increasingly larger contribution to a negative Grüneisen parameter.

The shock data of Nellis et al.[10]is plotted in figure 4. For the sake of clarity the calculated shock cooling trajectories were omitted. The dashed line defines the boundary separating the regions of the phase diagram over which the calculated Grüneisen parameter is predicted to be positive or negative[13]. The parameter crosses the bend in the Hugoniot near 10 Å^3. Nearby is an apparently out of line data point which, if correct, may provide some evidence for an liquid-liquid phase transition (LLPT). With increasing compression along the Hugoniot the second shocks lie at successively smaller volumes with successively smaller temperature rises. For volumes above 9 Å^3, γ is positive and reshocking leads to a modest temperature rise (points1,2 to1,2). Near 9 Å^3, the Grüneisen parameter is estimated to be zero, and there is little or no temperature change on reshocking (point 3 to 3). Near 7 Å^3, the negative Grüneisen parameter is negative and leads

to temperature lowering (points 4,5 to 4,5). The parameter is zero near 5.2 $Å^3$, the volume at which Eremets discovered a stable c-g polymer at 110 GPa, 7000 K and a volume of ~7.2 $Å^3$.

A comparison of the second shock volumes in figure 4, with the phase volumes in figure 2 is illuminating. It shows that with increasingly smaller volumes, the second shocks lie in energetically more stable regions of the phase diagram. In fact, the second shocks, 4 and 5, are near 7$Å^3$, the volume at which Eremets et al.[8] found the N_2 to cg-N transition to occur with a change from 6.7$Å^3$ to 5.2 $Å^3$. These results point to a conclusion that shock cooling in liquid nitrogen occurs when the second shock is driven into volumes near the molecular-polymer phase transition. This raises the possibility that the nonmetal-metal transition detected by Chau et al.[11] at 120 GPa and a volume of ~6.9 $Å^3$, near to the transition to the cg-polymer volume, represents the crossing of a first order liquid-liquid phase transition(LLPT).

C. Related theoretical studies

Van Thiel and Ree[14], and Fried and Howard[15], also reported calculations for shock compressed liquid nitrogen. They used models for liquid N_2 that are similar to ours. Their calculations assumed N_2 dissociated to 2N, and the N-N inter-atomic potential was fitted to reproduce the experimental data. However, the location of the energy minima defined in their effective potentials, r_m~2.5 Å, converts into a close-packed volume of 6.7$Å^3$/atom, closely approximating the locations of the minima in the polymer systems. Although theory[1-4] and experiment [5-8] appear to favor the presence of polymer-like structures their level of agreement with the experimental data is comparable to ours.

Mazevet et al. [16] performed molecular dynamic simulations for multiple-shocked liquid nitrogen. While their single-shock Hugoniot agrees well with the gas-gun experiments, calculations of the second shock showed that the temperature variation between the first and second shocks is smaller than found experimentally and close to zero. They found values of the Grüneisen parameters over the dissociating region to be near zero, but not negative. Although Mazavet et al. determined the N_2 dissociation fraction by performing cluster analysis at

each step over the whole trajectory, they do not report the distribution of monomers, dimers or larger molecules. While Mattson et al.[3] do report the presence of dimers and polymers they do not report fractional estimates of composition.

III. Nitrogen Hugoniot at P > 100 GPa.

With increasing shock pressure, to well above 100 GPa, molecular and polymeric nitrogen will dissociate to a dense plasma with atomic and ionic states of partial and complete ionization. Theoretical studies for liquids at less extreme conditions have typically employed models based on liquid perturbation theory with effective intermolecular potentials[12-15], or using density-functional-theory molecular dynamics [16]. However, with increasing temperature, the ability of these methods to predict the properties of dense fluids becomes increasingly unreliable due molecular dissociation and electron excitation.

A useful theoretical approach for treating dense plasma conditions is the Activity Expansion (ACTEX) method[17-18]. The starting point for the ACTEX program is the Coulomb interactions between all the fundamental constituents; i.e., electrons and nuclei, in the system in bound, scattered and free states. The standard procedure is to expand the non-ideal Helmholtz free energy in terms of two-body, three- body, etc., clusters i.e., a cluster expansion. The leading terms are,

$$\frac{F - F_o}{VkT} = S_R + \sum_{i,j} S_{i,j} + \sum_{i,j.k} S_{i,j,k}, \qquad (1)$$

where $S_R = \frac{1}{12\pi\lambda_D^3}$, is a Debye screening length,

and, $S_{i,j} = -n_i n_j \left[B_{i,j}(T,\lambda_D) + 2\pi \int_0 (1 - u_{i,j} - \frac{\partial u_{i,j}}{2}) r^2 dr \right]$.

$B_{i,j}(T,\lambda_D)$ is the second virial coefficient for the static screened potential. $u_{i,j}$ are the interaction potentials. Rogers and Young [17] have provided a more detailed description of each of the free energy terms, including $S_{i,j,k}$. The free energy is transformed into an activity expansion, in terms of pressure, that accounts for the formation of ions, atoms and molecules[[17,18] .

Pressure ionization results naturally from the effect of multi-particle Coulomb interactions on bound states, and without the introduction of *ad-hoc* assertions. As the density is increased there will be a continuous transition from atomic to delocalized states. This is a definite advantage over the chemical picture (free energy minimization) methods in current use, all of which introduce ad-hoc models to obtain these effects. Consequently, the thermodynamic properties are continuous functions of temperature and density. This method works very well for low to moderate density plasmas and for multiply ionized plasmas[18,19]. However, it is not easily extended to states where higher order corrections are required which places a lower limit to the pressures that may be reliably predicted. This drawback could be improved by employing standard liquid theory methods.

Figure 5 shows the experimental nitrogen Hugoniot with a smoothed interpolation connecting to the ACTEX calculations. The polymeric solid and liquid region below 100 GPa is indicated. The predicted Hugoniot exhibits a compression maxima at about V_O/V~5.3, near 1000 GPa (T~3.5 10^5 K) arising from the ionization of L shell electrons. V_O=34.7cm^3/mol.

The ionization of L shell electrons creates a system of Z= 5 ions bathed in a gas of electrons and a second compression maxima due to K shell electrons appears near Vo/V~5 and 4.10^4 GPa (T~ 2.3 10^6 K). With further increases in temperature the Hugoniot approaches the ideal gas limit near 10^6 GPa. Similar features appear in the case of metals where it has been shown that the ionization of tightly held inner K and L electron shells leads to compression maxima of approximately 5-6 fold [20]. For extremely strong shocks the compression approaches the ideal gas limit of V_O/V=4, where Vo is the volume of the initial state of the liquid. The present calculations neglect relativistic effects and radiation pressure which only become significant above 2.10^4 Mbar and 10^8 K and lead to an increase in the compressibility beyond fourfold.

IV. Discussion

By employing a theoretical model using shock data fitted to a hypothetical polymer, we have been able to make connections with recent theoretical and experimental studies in order to explain the origin of shock cooling in liquid nitrogen. Cooling occurs when the doubly shocked liquid is driven into a volume (~7 $Å^3$/atom) at 7000 K which are nearly the same conditions at which Chau et al.[11] measured electrical conductivities found a nonmetal-metal transition. And, the molecular solid transforms into the polymeric solid phase at 6.9 $Å^3$/atom[8]. These consistency of these different measurements point to the region of a phase change to polymers near V~7 $Å^3$/atom, sketched, near Vo/V=4, in figure 5.

In the case of phosphorous there has been the recent discovery of a first order liquid-liquid phase transition (LLPT) from a molecular tetrahedral P_4 phase to a "network" phase, near a pressure of 1 GPa, and extending up to 2500 K and 0.3 GPa[21,22]. The nature of the "network" phase is poorly understood, but is believed made of chained P_4 monomers, or polymers, flattened into a "butterfly" shape [23,24]. It is worth noting that at a pressure above 1 GPa the melting curve of phosphorous decreases with increasing temperature, evidence of a negative Grüneisen parameter. However, there is no evidence from electrical conductivity measurements for a discontinuous change that would imply a first order change in nitrogen. Instead the electrical conductivity increases monotonically with increasing pressure from 80 to 110 GPa, and remains constant to 180 GPa at a metallic-like value of 1000 $(Ohm\text{-}cm)^{-1}$. Other low-Z systems, such as CO_2 that polymerizes into an extended covalent solid may also exhibit shock cooling[25].

At the present time, only double shock and quasi-isentropic multiple shock experiments are likely to provide additional information about the nature of dense liquid nitrogen in the 50-100 GPa range and temperatures above 5000 K. Since these experiments are difficult, a theoretical program based on *ab-initio* simulations, using the best available exchange and correlation functions, would be helpful.

In pressure regime above 100 GPa, where experimental information is now lacking, the possibility for acquiring such data for nitrogen lies in the realm

of the recently developed high energy density experimental shockwave methods [26,27]. The calculations reported here may provide a useful guide for these experiments.

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Figure Captions

Figure 1. Nitrogen Hugoniot (open circles) and reflected shock points (filled circles), plotted versus pressure versus temperature [9,10]. Numbers show corresponding first and second shocks.

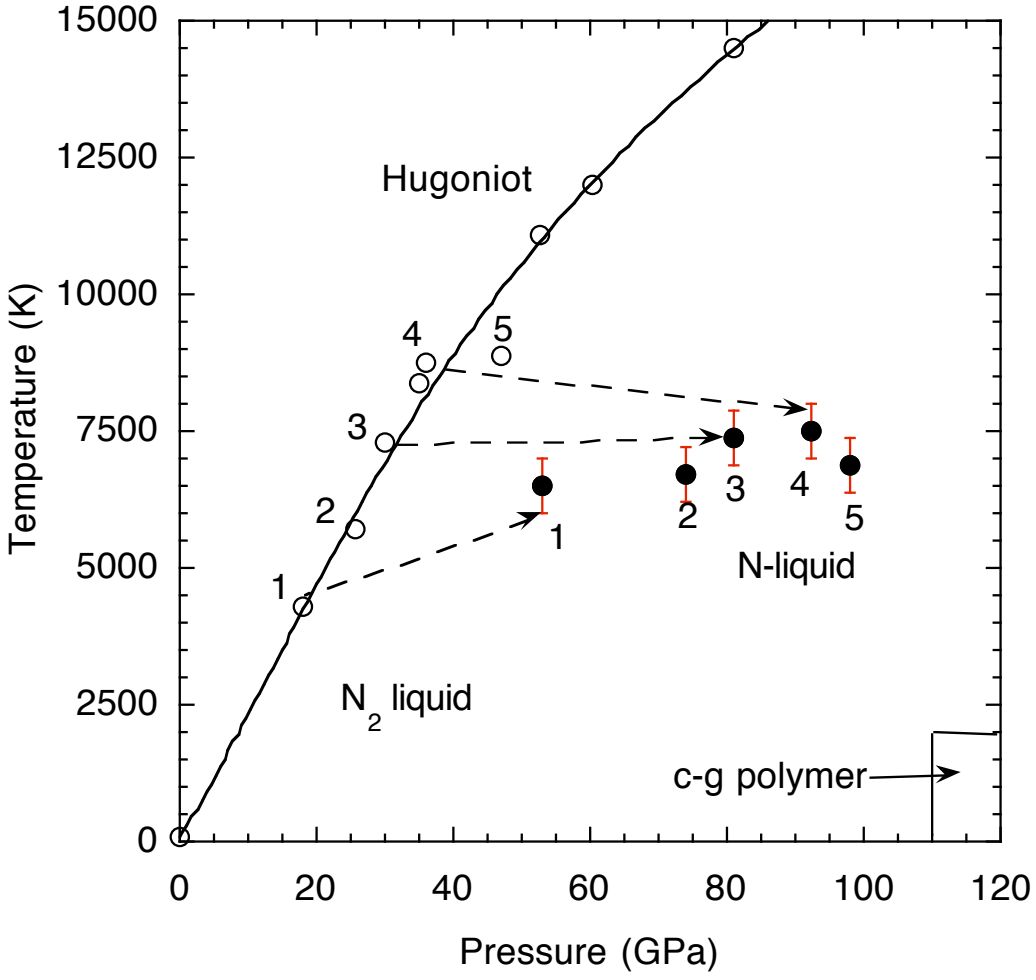
Figure 2. Nitrogen phases. Curves labeled N2, c-g and A7 were taken from Mailhoit et al. [2]. N-"polymer" curve was obtained from the fit to shock data.

Figure 3. Pressure-volume equation of state data at 300 K reported by Eremets et al.[8] and model calculations(solid lines).

Figure 4. Nitrogen Hugoniot (open circles) and reflected shock points (filled circles), plotted volume versus temperature [10]. Numbers show corresponding first and second shocks. Dashed curve is the boundary separating the regions over which the calculated Grüneisen parameter is predicted to be positive or negative[13].

Figure 5. Nitrogen Hugoniot to extreme conditions. Experimental data (filled circles)[10], connected to ACTEX calculations (solid curve) by a smoothed interpolation (long-dashed curve). The short-dashed line denotes, roughly, the location of a possible LLPT.

Fig. 1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Hugoniot
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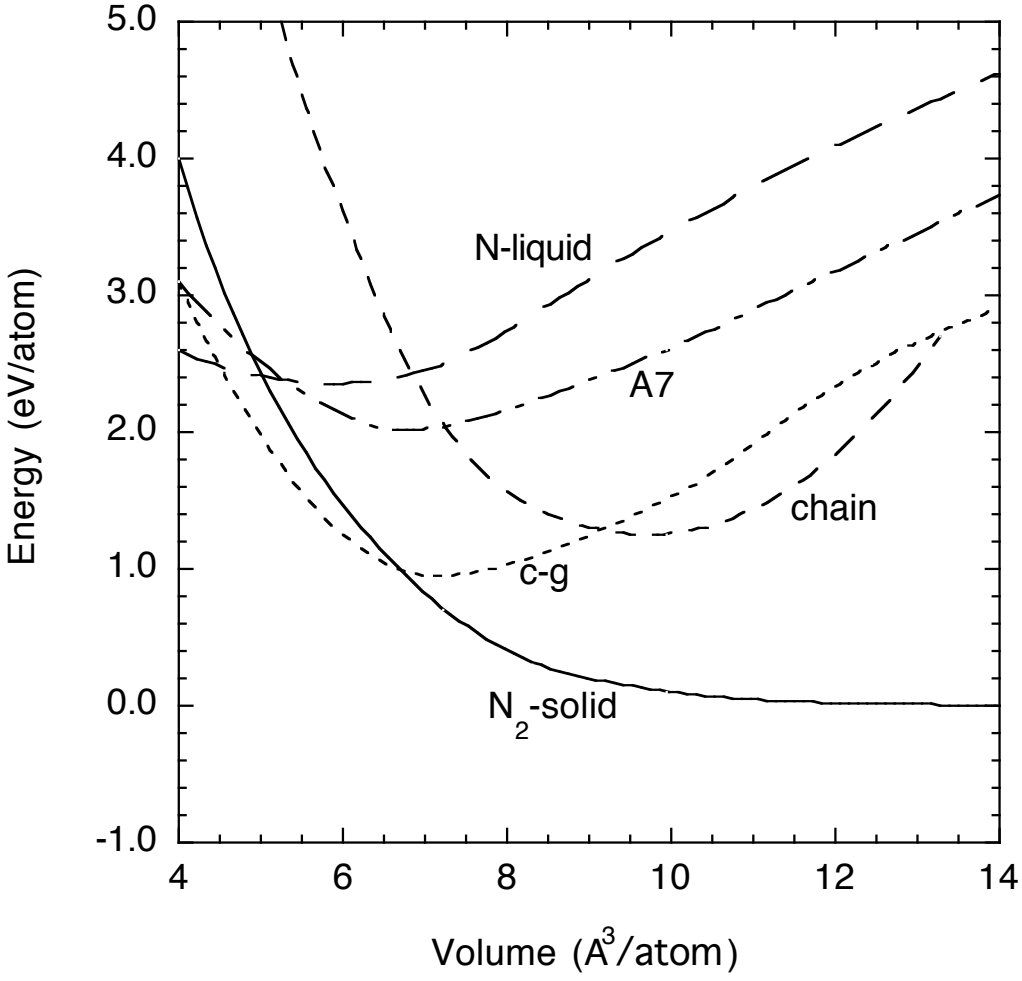
N2 liquid
N-liquid
c-g polymer

Fig. 2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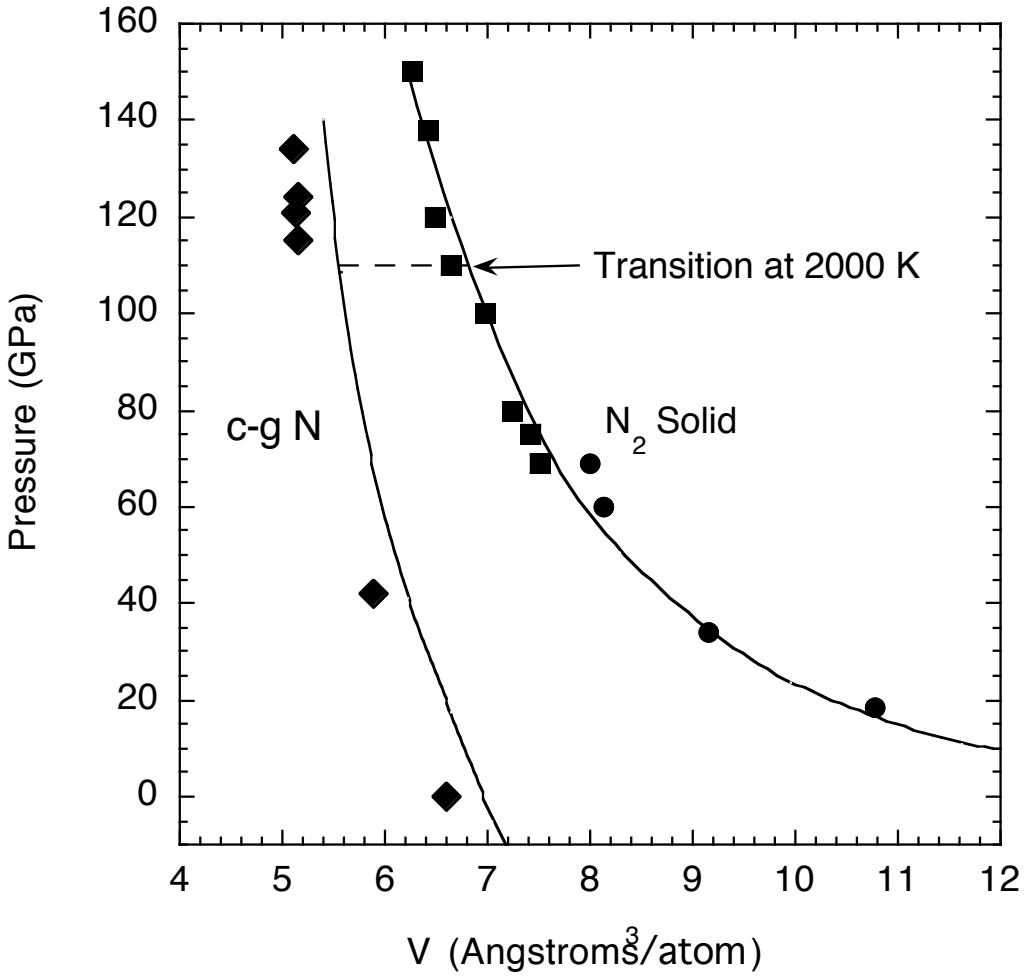
A7
chain
c-g
N2-solid

Fig. 3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V (Angstroms3/atom)
Transition at 2000 K
c-g N
N2 Solid

Fig. 4

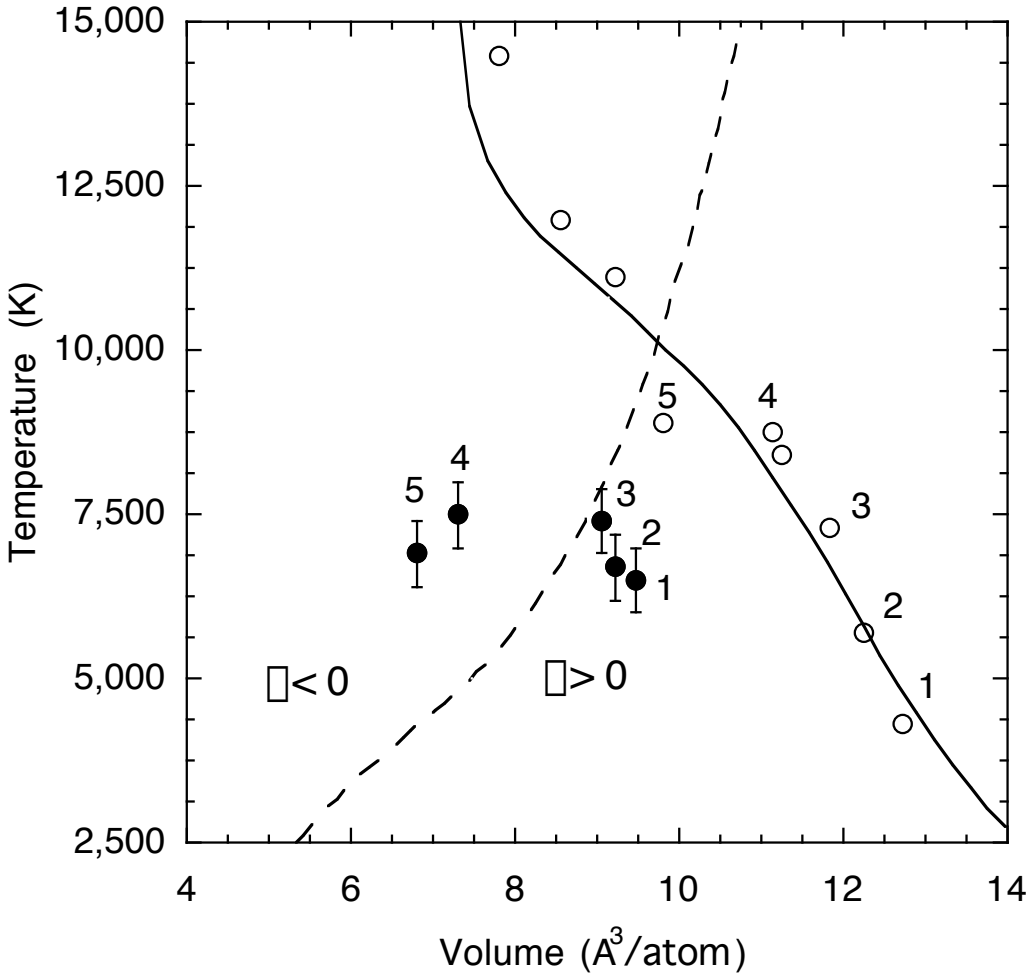
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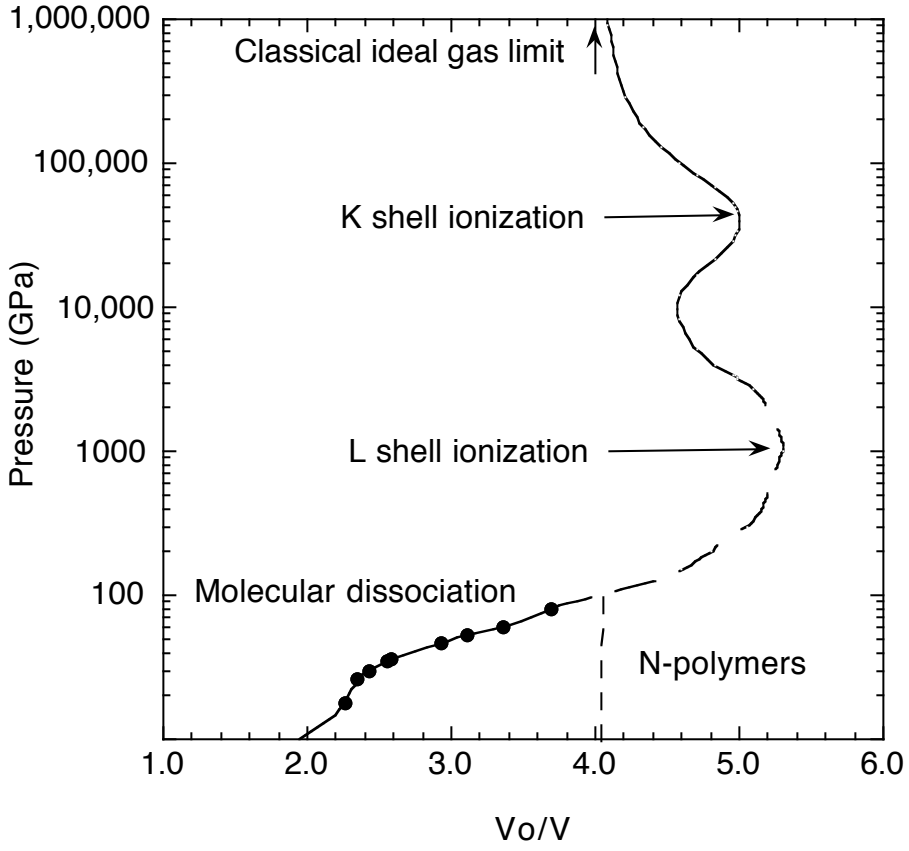
Fig. 5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4.0
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6.0
Vo/V